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Absorption of carbon dioxide in a bubble plate tower

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Department:

ABSORPTION OF CARBON DIOXIDE IN A BUBBLE PLATE TOWER

BY

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THESIS

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A debt of gratitude is due Dr. F. H. Conrad in directing and guiding this work and to the various members of the department who willingly gave their assistance.

W. A. E.

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INTRODUCTION

Gas absorption, one of the chief operations of chemical engineering, has occupied investigators for a long time. Results of many experiments on the general subject of gas absorption have been published. However, relatively few data have appeared in the literature on the use of bubble cap towers for gas absorption although they constitute one of the three major classifications of absorption equipment. Bubble cap towers are used extensively in the petroleum industry. More performance data would increase the versatility of existing equipment.

The Chemical Engineering Department of the Missouri School of Mines and Metallurgy possessed a twelve plate column which had been used for distillation. It seemed desirable to set this up as a gas absorption unit with two objects in view. First, the resulting piece of equipment could be used for experimentation on gas absorption for the course in chemical engineering laboratory. Second, an investigation could be carried on with the apparatus to determine its performance, to check on the very low values of efficiencies which are reported for this type of apparatus, and to compare the performance with other types of equipment.

The variables affecting the rate of gas absorption

and hence the performance of equipment have been investigated at considerable length, but recently Killeffer[1] and others have suggested that the surface tension of the absorbing liquid may have an important effect upon the rate of gas absorption. In view of the introduction of newer wetting agents, especially Aerosol O.T.[2], which give tremendous lowering of surface tension, it was desired to make a preliminary investigation of this effect.

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1. Killeffer, D.H., "Absorption of Carbon Dioxide", Ind. Eng. Chem., 29, 1293 (1937)

2. American Cyanamid and Chemical Company

PREVIOUS WORK

Since the introduction of the two film theory of Whitman and Lewis[1], great strides have been made in expressing quantitatively the rate of absorption of a gas by a liquid. Hanks and McAdams[2] absorbed NH_3 in water with a small laboratory wetted-wall tower. Kowalke, Hougen and Watson[3] and Chilton, Duffey and Vernon[4] used packed towers up to one foot in diameter to absorb NH_3 in water. They determined the variation of the absorption coefficient with height of packing, NH_3 concentration, liquid and gas rate, and temperature. Haslam, Hershey, and Kean[5] and Hixson and Scott[6] absorbed both NH_3 and SO_2 in water using

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1. Lewis,W.K., and Whitman,W.G., "Principles of Gas Absorption", Ind.Eng. Chem., 16, 1215-20 (1924)

2. Hanks,W.V., and McAdams,W.H., "Studies in Absorption"., Ind. Eng. Chem., 21, 1034-9 (1929)

3. Kowalke,O.L., Hougen,O.A., and Watson,K.M., "Absorption of Ammonia in Towers", Chem. Met. Eng., 32, 443-6 (1925)

4. Chilton,T.H., Duffey,H.R., Verhon,H.C., "The Absorp- of Gases in Packed Towers", Ind. Eng. Chem., 29, 298-301 (1937)

5. Haslam,R.T., Hershey,R.L., and Kean,R.H., "Effect of Gas Velocity and Temperature on Rate of Absorption", Ind. Eng. Chem., 16, 1224-30 (1924)

6. Hixson,A.W., and Scott,C.E., "Absorption of Gases in Spray Towers", Ind. Eng. Chem., 27, 307-14 (1935)

small glass towers. The latter also reported runs using straw oil to absorb benzene vapors as did Simmons and Long[1].

The absorption of carbon dioxide has been much more extensively investigated. Hirst and Pinkel[2], among others, used the organic amines which form the basis of the Girbotol Process[3].

Due to its great industrial importance, the most work has been done on the use of alkaline carbonate or hydroxide solutions to absorb carbon dioxide. Notable among those employing batch operation is Hitchcock,[4 5 6] who used the carbonates and hydroxides of potassium, sodium and lithium. He investigated the variation of the rate of absorption with concentration. Continuous

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1. Simmons,C.W., and Long,J.D., "Tower Absorption Coefficients", Ind. Eng. Chem., 22, 718-21 (1930)

2. Hirst,L.L., and Pinkel,I.I., "Absorption of Carbon Dioxide by Amines", Ind. Eng. Chem., 28, 1313-15 (1936)

3. Wood,W.R., and Storrs,B.D., "Girbotol Purification Process", Am. Pet. Inst. Proc., 19M (111) 34, My. (1938)

4. Hitchcock,L.B., "Rate of Absorption of CO_2", Ind. Eng. Chem., 26, 1158-67 (1934)

5. Hitchcock,L.B., and Cadot,H.M., "Rate of Absorption of CO_2", Ind. Eng. Chem., 27, 728-32 (1935)

6. Hitchcock,L.B., "Mechanism of Gas Liquid Reaction", Ind. Eng. Chem., 29, 302-8 (1937)

counter-current absorption in packed towers was carried out by Comstock and Dodge[1] and Williamson and Mathews[2] who scrubbed the gas with carbonate solutions. They determined the effect of concentration, temperature, and liquid and gas flow rates.

Because of its lesser industrial importance, the investigation of water as an absorbant has not been as extensive. Sherwood, Draemel, and Ruckman[3] report the desorption of CO_2 from water in a packed tower 18 inches in diameter and 51 inches high. Payne and Dodge[4] and Cantelo, Simmons, Giles, and Brill[5] employed small laboratory scale towers packed with rings to absorb CO_2 in water. The former gave an excellent review of the literature. The latter

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1. Comstock,C.S., and Dodge,B.F., "Rate of CO_2 Absorption by Carbonate Solutions in a Packed Tower", Ind. Eng. Chem., 29, 520-9 (1937)

2. Williamson,R.V., and Mathews,J.H., "Rate of Absorption and Equilibrium of CO_2 in Alkaline Solutions", Ind. Eng. Chem., 16, 1157-61 (1924)

3. Sherwood,T.K., Draemel,F.C., and Ruckman,N.E., "Desorption of CO_2 from Water in a Packed Tower", Ind. Eng. Chem., 29, 282-5 (1937)

4. Payne,J.W., and Dodge,B.F., "Rate of Absorption of CO_2 in Water and Alkaline Media", Ind. Eng. Chem., 24, 630-7 (1932)

5. Cantelo, et al, "Tower Absorption Coefficients", Ind. Eng. Chem., 19, 989-97 (1927)

reports exceptionally high efficiencies. Davis[1] reported upon the rate of absorption using batch apparatus.

Bubble plate towers used in commercial rectification have over-all plate efficiencies of 65% to 95%; however the efficiencies of this type of equipment when used for absorption are reported to be much below these values. Atkins and Franklin[2] report 18% for petroleum equipment. Whitman and Davis[3] absorbed carbon dioxide in a 15 plate tower with one bubble cap per plate using sodium carbonate solution as an absorbant. The usual graphical methods indicate that their tower performed the work of one theoretical plate or an efficiency of less than 7%. Sherwood[4] reports the work of Reynolds and Sanders[5] who absorbed NH_3 in water in a single plate tower.

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1. Davis,H.S., "Initial Absorption Rates of CO_2 by Water and Dilute Sodium Carbonate Solutions", Ind. Eng. Chem., 25, 1023-25 (1933)

2. Atkins,G.T., and Franklin,W.B., Refiner 15, 1 p. 30 (1936)

3. Whitman,W.G., and Davis,G.H.B., "A Comparison of Gas Absorption and Rectification", Ind. Eng. Chem., 18, 354-6 (1926)

4. Sherwood,T.K., "Absorption and Extraction", New York, McGraw-Hill, 1937, p. 191

5. Reynolds,B.M., and Sanders,F.W., Thesis. Cambridge, Mass., M.I.T., 1931

They obtained a Murphree efficiency of 65-85%, averaging 75%. McCabe and Swanson[1] used lime solution to absorb SO_2 in a bubble plate tower and obtained an efficiency of only 55%, even though the liquid height on each plate was two feet. Goosmann[2] in a long dissertation on carbon dioxide, compared the efficiencies of bubble cap and packed towers as percentage of incoming CO_2 absorbed, using Na_2CO_3. Tables indicate qualitatively a greater efficiency for bubble towers, however, the towers were operating under different conditions, and dimensions and descriptions of them were omitted. In view of the foregoing data the work described in this paper was undertaken.

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1. McCabe,W.L., and Swanson,W.H., "The Paulson Acid Absorber", 92, No. 26, p. 48-50 (1931)

2. Goosmann,J.C., "CO_2 in Its New Field of Usefulness", Ice. and Refrig., 79,[2]399 (1930)

ABSORPTION THEORY

The transfer of gas molecules from the gas phase into the liquid phase is a diffusional process and the rate is proportional to a driving force and a resistance. The analogy to the flow of electricity and fluid flow has often been pointed out. The resistance to gas absorption is the result of two, more or less stagnant, or perhaps better, laminar films - one on either side of the interface - the liquid film and the gas film[1]. It is reasonable to assume that at the actual interface, equilibrium is reached; that is, the partial pressure of the solute gas at the interface is equal to the vapor pressure exerted by that component from the liquid at the interface. If y designates the concentration of the solute gas in the main body of the gas stream and y_i, at the interface, then $y - y_i$ is the driving force across the gas film. In a similar manner if x and x_i are the concentrations of the solute gas in the liquid phase in the main body of the liquid at the interface respectively, then $x_i - x$ is the driving force across the liquid film. Setting up an equation

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1. Lewis,W.K., and Whitman,W.G., "Principles of Gas Absorption", Ind. Eng. Chem., 16, 1215-20 (1924)

for the rate of transfer:

$$N = k_g(y - y_i)\,A = k_l(x_i - x)A$$

Where N = lb. mols. of solute gas transferred per hour.

A = interfacial area in square feet over which absorption is taking place.

k_g = gas film coefficient, lb. mols. per sq. ft. per hour per unit of driving force in mols. solute gas/mol. of inert gas.

k_l = liquid film coefficient, lb. mols. per sq. ft. per hr. per unit of driving force in mols. solute per mols. solvent.

y = mols. solute gas/mol. inert gas in main gas stream.

y_i = mols solute gas/mol inert gas at interface.

x = mols solute/mol solvent in main body of liquid.

x = mols solute/mol solvent liquid at the interface.

In the case of a slightly soluble gas such as CO_2 in water, most of the resistance to diffusion is in the liquid film; that is, the value of y_i becomes very nearly equal to y and x_i nearly equal to x_e, the equilibrium value corresponding to y. Now, by using an

over-all coefficient K_L (since Henry's Law applies), the equation becomes:

$$N = K_L (x_e - x) A \qquad (2)$$

Now if we consider continuous counter-current absorption[1, 2] in a tower such as that sketched in figure 1, and if:

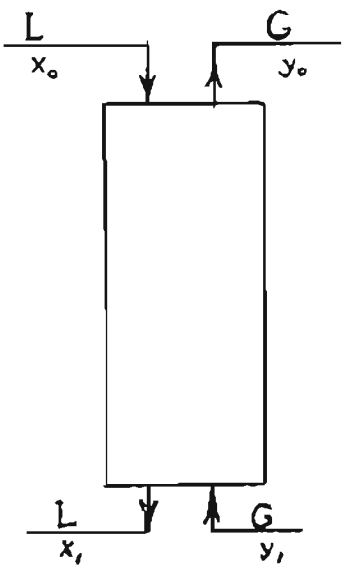
L = lb. mols of solvent entering per hour

G = lb mols inert gas/hour

V = volume of tower in cubic feet.

a = interfacial area in square feet/cubic feet of tower.

Figure 1.



A material balance may be set up over any section of the tower.

$$Gdy = Ldx = N \qquad (3)$$

and since A = a V, by sub. in equation (2)

$$N = K_L a(x_e - x)\, d\, V \qquad (4)$$

Therefore:

$$L\, d\, x = K_L a\, (x_e - x)\, d\, V \qquad (5)$$

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1. Fiss,E.C., "The Design, Construction, and Operation of a Carbon Dioxide Absorption Tower". Thesis. Atlanta, Ga., Georgia School of Technology. 1938.

2. Sherwood,T.K., "Absorption and Extraction", New York, McGraw-Hill p 95

Rearranging:

$$\int_{x_o}^{x_1} \frac{d\,x}{(x_e - x)} = \frac{K_L a}{L} \int_{0}^{V} dV = \frac{K_L a V}{L} \qquad (6)$$

$K_L a$ is evaluated as one figure, the so called over-all volumetric coefficient in mols absorbed per hour per cubic foot per unit of driving force. The expression, $\int_{x_o}^{x_1} \frac{d\,x}{(x_e - x)}$, can be evaluated by graphical integration. The driving force is obtained from the operating line and the equilibrium line, plotted as y against x. The equation of the operating line is obtained from equation (3), using the terminal conditions of the tower.

$$G(y_1 - y_o) = L(x_1 - x_o) \qquad (7)$$

The usual graphical method envolving the theoretical plate[1] will also be employed to analyze the results.

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1. Sherwood, T.K., "Absorption and Extraction", New York, McGraw-Hill, 1937 p. 82

CONSTRUCTION OF THE UNIT

The tower proper, which had previously been used for distillation, contained twelve plates; the bottom six were placed five inches apart and the top six, four inches. The inside diameter was 7 7/8 inches. Each plate contained one bubble cap, 4½ inches in diameter. Figure 2 shows a sketch of the unit and figure 3 is a dimensioned drawing of a plate. The construction was of copper with a tin lining.

The auxillary equipment which had to be built was affected by the system chosen and by the method of operation, continuous (recycling) or intermittant. It was at first considered desirable to use the ethanol amines, due to recent developments employing them to absorb acid gases. However corrosion problems as reported by Gregory and Scharmann[1], especially in the case of copper and tin, prevented their use. Since the bubble plate tower is especially adapted for cases where the liquid film is controlling, it was decided to use a slightly soluble gas. For practical purposes the choice was almost limited to CO_2.

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1. Gregory,L.B., and Scharmann,W.G., "Carbon Dioxide Scrubbing by Amine Solutions", Ind. Eng. Chem., 29, 514-19 (1937)

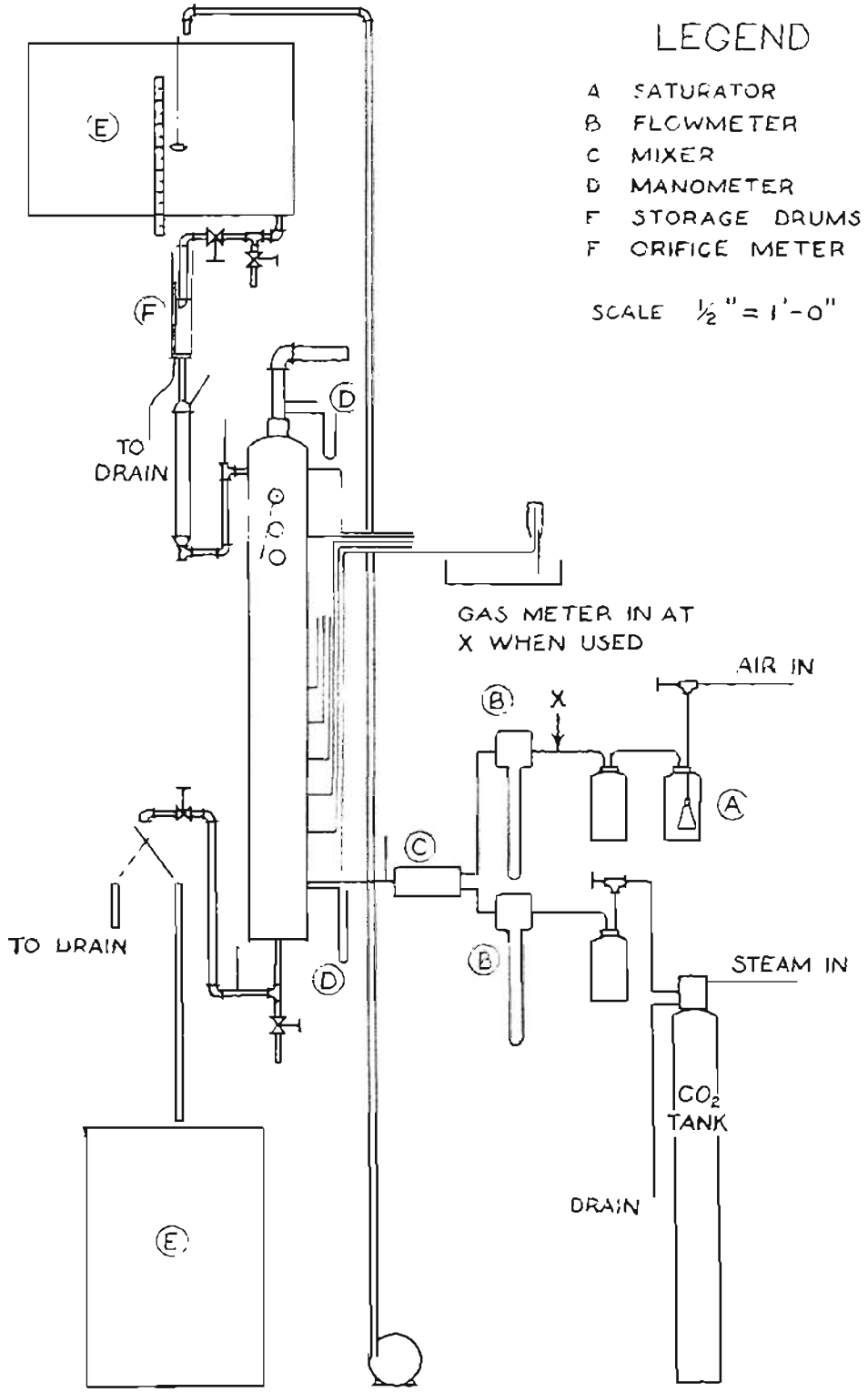


FIG. 2 GENERAL LAYOUT

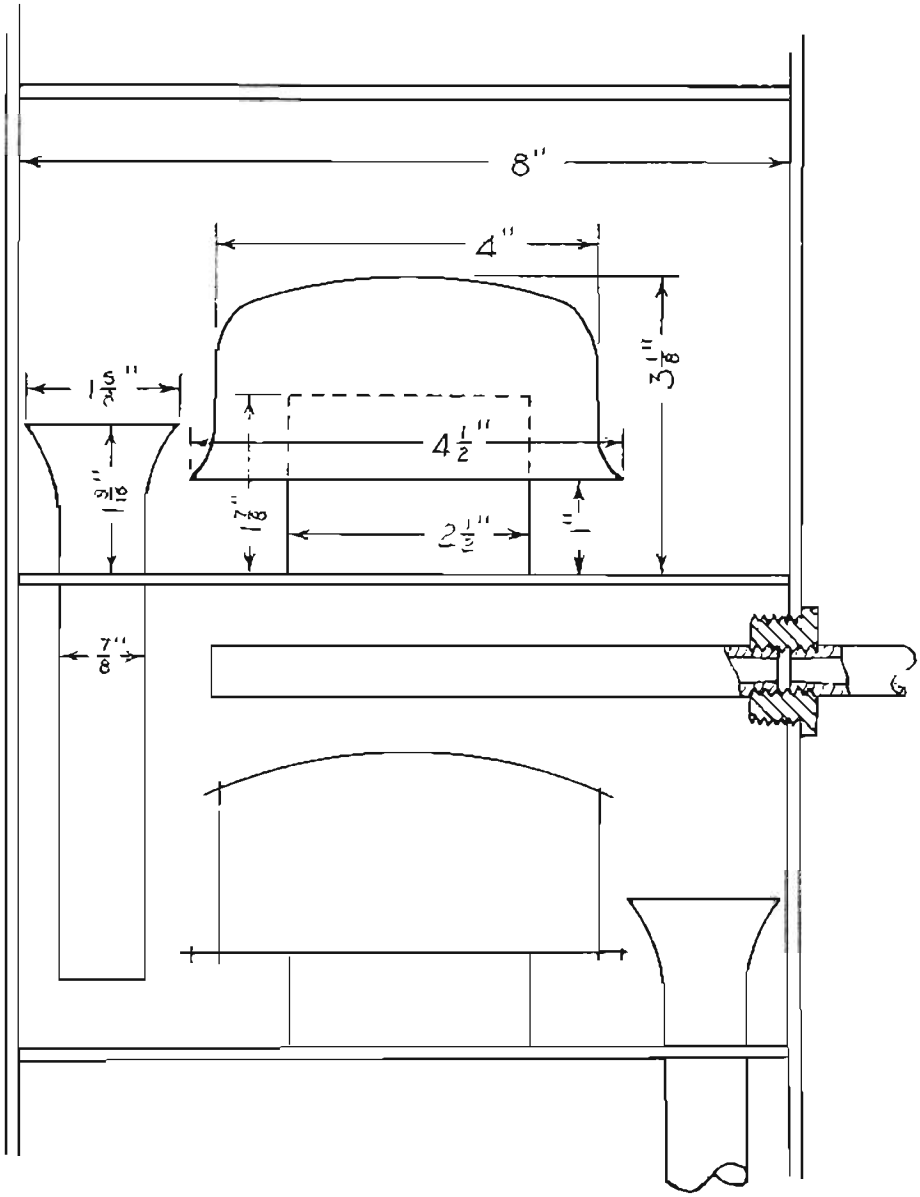


FIG. 3 TYPICAL PLATE AND BUBBLE CAP

The question arose whether to generate the CO_2 by burning pentane from the school gas lines or whether to use the liquified form in commercial tanks. Assuming 100% complete combustion, CO_2 could be obtained by burning pentane at a cost of 1.12 cents per pound. The liquid form could be obtained for 13.5 cents per pound. In view of the additional equipment which would be required, such as a blower to obtain the necessary pressure, the difficulty of operating a burner, the non-uniform pressure of the gas lines, and its unavailability on other than school days, gas in commercial tanks was chosen. Later calculations have shown that approximately 0.0003 pound mols of CO_2 are used per minute during the average run. Assuming 45 minutes for the average operating time, 0.0003 x 45 x 44 = 0.594 pounds of CO_2 per run or a cost of only 8.02 cents per run.

To eliminate a reboiler and cooler it was decided to run intermittently. To further simplify operation and analysis, distilled water was used as an absorbant in most of the runs. A 55 gallon drum was mounted above the tower to supply water during the run. A float device indicated the level in the drum. An orifice discharging vertically downward was incorporated in a simple constant rate device on the liquid

line to the tower. The rate for such an orifice varies only slightly with the head. Figure 4 is a sketch of the metering system. The overflow tube maintained essentially a constant head. The vent below the orifice was necessary to maintain atmospheric pressure on the down-stream side. An advantage of this device is that various sized orifices can be made up and interchanged readily. The goose-neck acted as a liquid seal to prevent gas from escaping.

Air from the line was regulated by a needle valve, passed through a saturater as shown in figure 2, then through another bottle to remove entrainment, and then through a flow meter. Carbon dioxide was expanded first through the tank valve and then through a specially constructed needle valve made from the base of a Fisher burner. During the first runs, difficulty was encountered in maintaining a constant flow due to the CO_2 tank valve freezing. To prevent this difficulty a few feet of copper tubing were bent into a five inch coil with seven turns around the valve and the whole coil was encased in sheet metal. By passing steam through the coil most of the trouble with the valve was eliminated.

A large bottle in the carbon dioxide line before the flow meter helped smooth out minor irregularities. A Sargent Wet Test Meter was calibrated and a factor

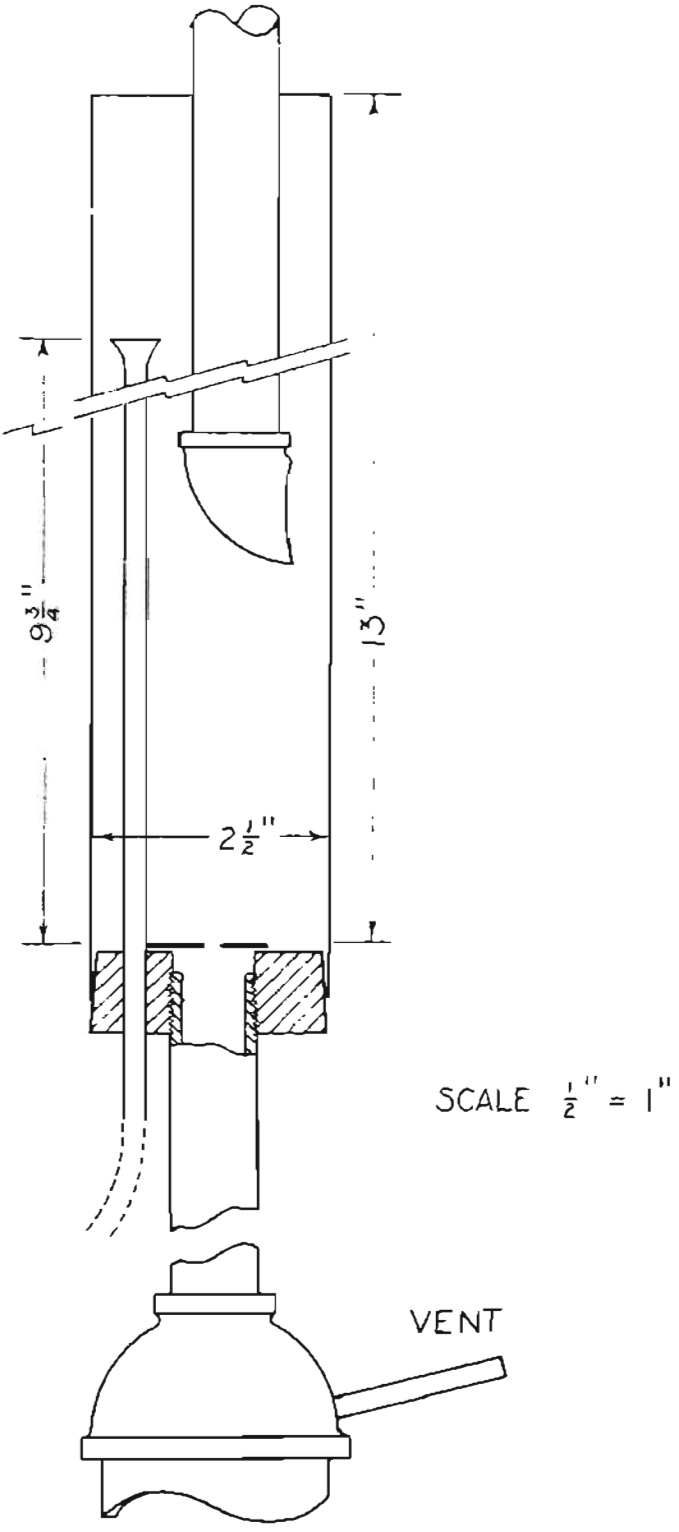


FIG. 4 LIQUID ORIFICE METER

of 1.027 obtained. This was in turn used to obtain the calibration curves in figures 5 and 6 for the gas flow meters. After metering, a small metal cylinder 4 x 9 inches packed with Berl saddles was used as a mixing chamber. From this the gases were lead directly to the base of the tower.

After the tower had been set up, air was blown into the gas inlet with all the plates filled with water. The pressure in the bottom section was measured with a mercury manometer to be 0.7" Hg. From this, the height of the liquid leg necessary to maintain this pressure and to prevent gas from escaping with the exit liquor was calculated to be 9.5 inches.

Before actually putting in pipe lines it was advisable to determine the flooding rate of the tower in order to know the maximum quantity which they would be required to carry. This rate was first calculated assuming each downcomer to act as an orifice. Since the distance between plates in the upper section was four inches and the downcomer extended 1 9/16 inches above the plate, the maximum head on the "orifice" would be 2 7/16 inches or 0.12 feet. Using the formula:

$$V = A\,C\sqrt{2\,g\,H}$$

$$V = \frac{(.875)^2}{144 \times 4} \times 0.61 \quad 2 \times 32.2 \times 0.12 =$$

$$0.0071 \text{ ft.}^3/\text{sec.}$$

FIG. 5

CALIBRATION CURVE FOR

CO_2 MANOMETER

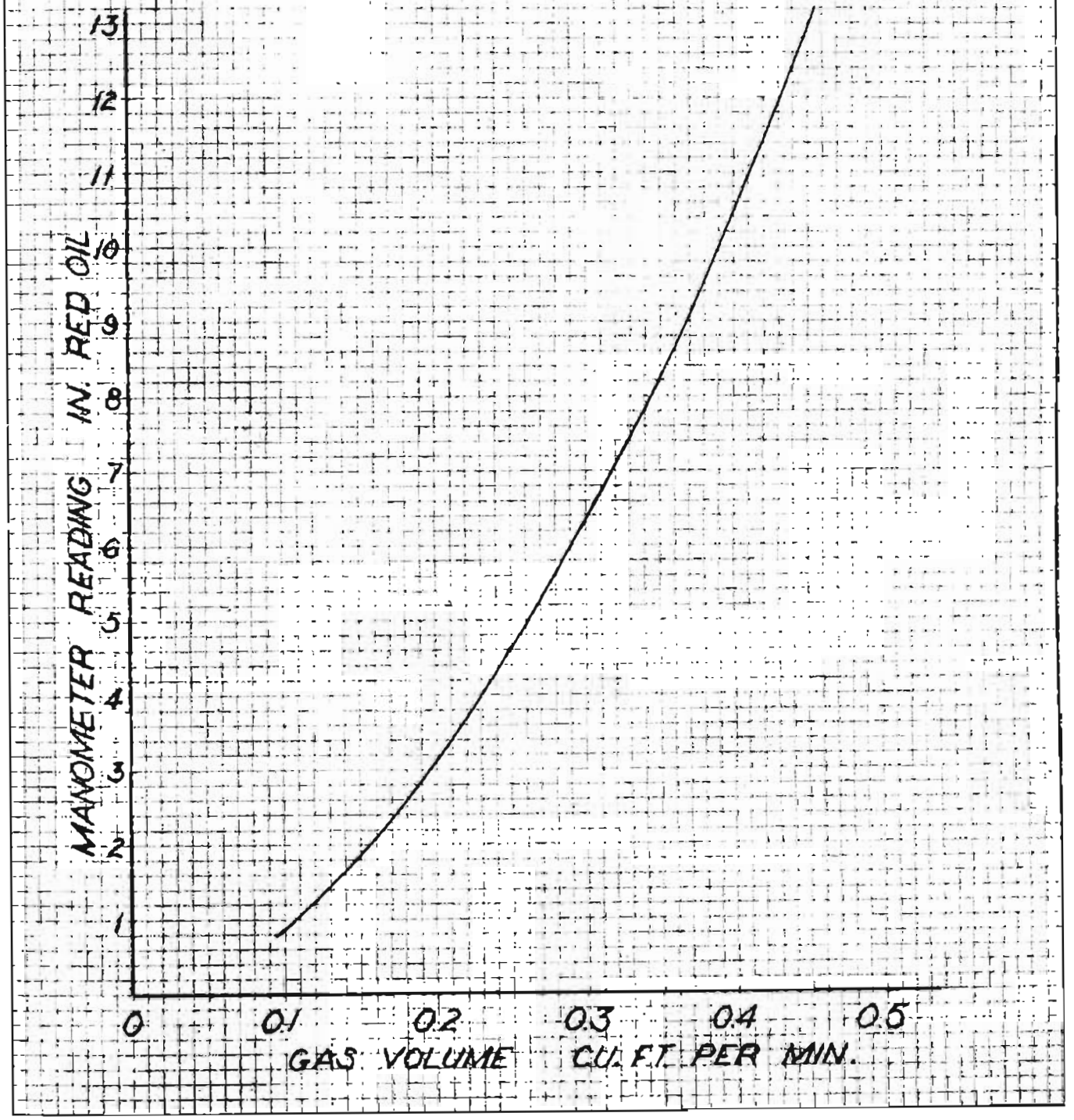
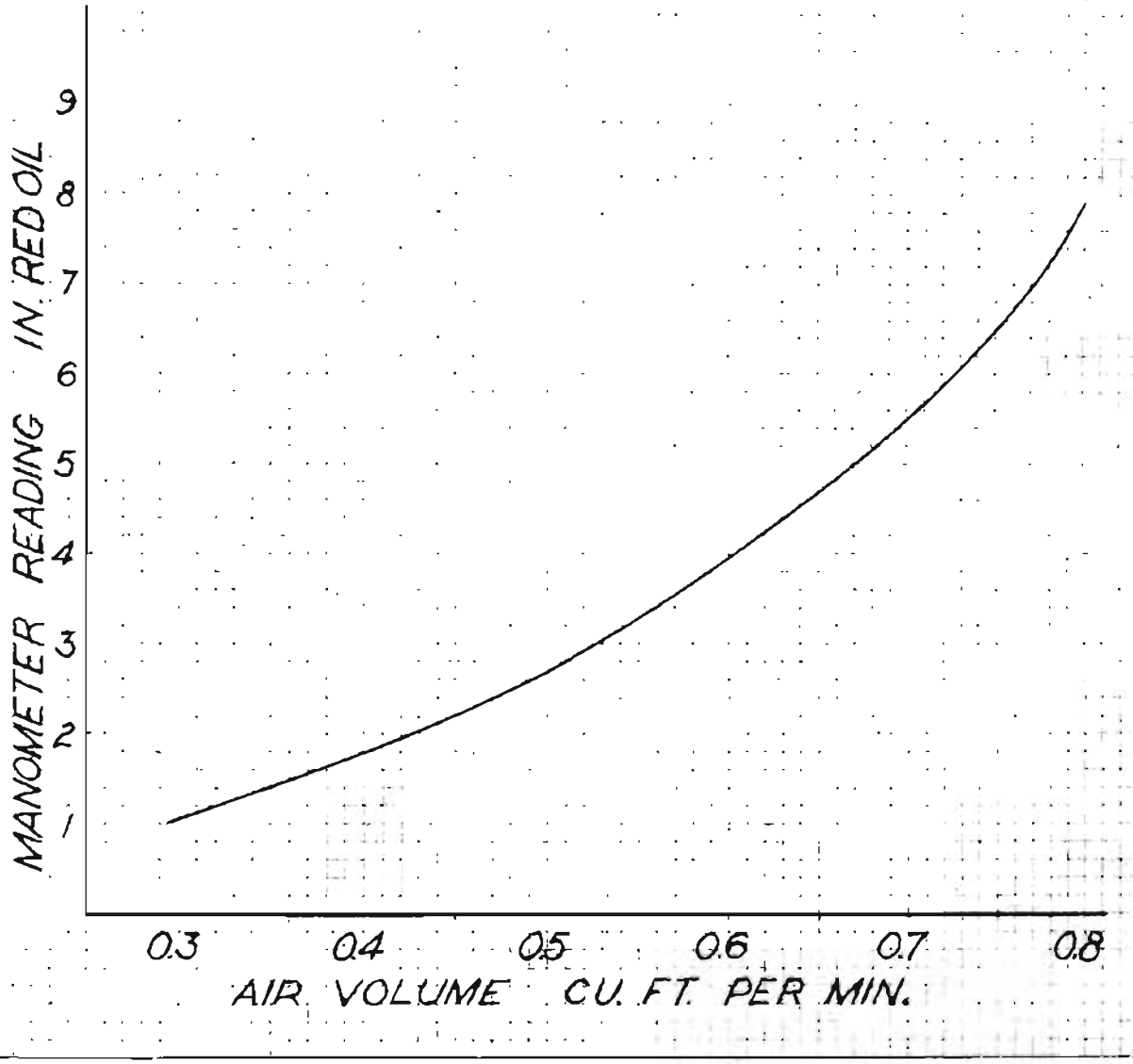


FIG 6

CALIBRATION CURVE FOR
AIR MANOMETER



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$0.0071 \times 60 = 0.426$ ft^3/min. or 26.6 lbs./ min

Water was then run down the tower, and the discharge weighed. A value of 84.4 lbs/minute was obtained in this manner. This indicated that liquid was also coming down the gas risers. Air at 10 lbs. per square inch was blown into the gas inlet at the base of the tower and the flooding rate redetermined with gas passing up the tower. In this manner the flooding rate, under operating conditions, was found to be 38.87 lbs./minute, (0.625 ft^3). Since the top of the downcomers were "bell-shaped", their discharge coefficient was larger than 0.61, the value assumed in the above calculation. With an inside diameter of eight inches the cross-sectional area was 0.349 ft^2. Hence the flooding rate can be expressed as 111.0 lbs./ minute/square foot of cross-sectional area.

Assuming a maximum flow of five feet per second we can calculate the pipe diameter required:

$$\frac{(D)^2}{144 \times 4} \times 5 = \frac{0.625}{60} = 0.0104$$

D = 0.62 inches ∴ 3/4" pipe will be ample

Outlets for liquid samples from each plate had been already installed. One quarter inch bronze needle valves were attached to draw off sample. Since it was desired to measure gas concentration at

any point, gas sampling tubes were installed in the vapor space above each plate. These tubes consisted of ¼ inch pipes, extending three fourths of the way across the inside diameter of the tower, and were drilled with a series of holes along the bottom. They were screwed into a ¼" to ⅜" bronze bushing which was in turn screwed and soldered to the copper shell. A ¼" bronze needle valve was attached to the bushing. This is sketched in figure 3 . Gas samples could be drawn directly into a gas burette or conducted through small glass tubing and collected over water.

An electrically driven (1/3 H.P.) centrifugal pump was employed to pump the water from carboys or to the lower storage drum to the feed drum above the tower. Thermometers were placed so that the inlet and outlet gas temperatures and inlet and outlet liquid temperatures could be measured.

OPERATION

Since the technic was changed continuously during the experimental runs, a detailed description of the final method of operation and duties of the various operators will be given at the end of this section.

Briefly, the gas flow and liquid flow were started nearly simultaneously. Gas flow was maintained at a constant value by manual control, using the flow meters as guides. Successive samples of the outlet gas indicated that the tower attained equilibrium after operating continuously for fifteen to twenty minutes. Gas samples were collected in wide mouth bottles of 130 ml. capacity, inverted in a water bath. Liquid samples were drawn into small 30 ml. bottles and stoppered immediately. Temperature, pressure, and flow meter readings were taken continuously throughout the run. After the first few runs, a Sargent Wet Test meter was placed in the gas line.

The liquid samples were analyzed by adding 25 ml. to 10 ml. of standard barium hydroxide. The excess hydroxide was back titrated with hydrochloric acid using phenolphthalein. The gas samples were displaced into a gas burette and the carbon dioxide absorbed in

a Hempel pipette using potassium hydroxide. The confining liquid for displacing the gas, as well as that used in the collecting bath, was an acidified solution of sodium sulfate as suggested by Kobe and Williams[1]. This was later changed to distilled water for the sample collecting and mercury was used as a confining liquid.

RUNS ONE TO FIVE.

The gas and liquid rates were adjusted to equal approximately the mean of the ranges employed by previous investigators. The liquid orifice delivered 4.604 pounds of water per minute. With the CO_2 flow meter at 1.0 inch of "red oil" (sp. gr. = 0.827) and the air meter at 1.5 inches, 0.00129 pound mols[2] of total gas entered per minute, (0.774 mols per hour), with a CO_2 content of about 22 per cent by volume.

These runs showed that the liquid analyses were much better than the gas analysis. A plot of liquid concentration against plate number gave a reasonably

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1. Kobe, K.A., and Williams, J.S., "Confining Liquids for Gas Analysis", Ind. Eng. Chem., 7, 37-8 (1935)

2. Throughout this paper "mols" will mean pound mols unless otherwise stated.

smooth curve. On the other hand, the gas analysis varied erratically and showed no trend with plate number. The gas analysis in run number five was nearly constant, 21.3 per cent with a maximum deviation of 0.7 per cent from this average.

Calculations based on the liquid analysis for this run showed that a total of 0.001294 mols of CO_2 were absorbed per hour. If the inlet gas is taken to be 21.2 per cent CO_2 as analyzed, a material balance requires that the outlet gas be 19.7 per cent CO_2. In an attempt to get a better correlation of gas concentration with plate number, it was decided to increase the amount of carbon dioxide absorbed. This could be most effectively accomplished by increasing the liquid rate as the coefficient of absorption is increased with increased liquid rate. Also the greater amount of scrubbing medium will increase the amount of absorption.

RUNS SIX TO ELEVEN

As indicated by the previous runs, a larger orifice delivering 11.83 pounds of water per minute was placed in the inlet liquid line. The strength of the standard barium hydroxide and hydrochloric acid solutions used in analyzing the liquid samples was

reduced from 0.1 normal, which was found to be too high, to 0.05 normal. Also to eliminate the difficulty with the sodium sulfate confining liquid, the gas samples were drawn directly from the tower into a gas burette and analyzed immediately.

Calculations based on the liquid analysis of run six shows that 0.00260 mols of carbon dioxide per hour were absorbed. However, the gas analysis and rate for the same run show a loss of 0.00588 mols per hour, or an error of over 100%.

The remainder of the runs in this set were devoted to discovering the error in the set-up, and obtaining a material balance that would check within the limits of engineering accuracy.

First, the inlet orifice was recalibrated and the original value checked. Likewise, the Sargent Wet Test meter, which had been placed in the exit gas line to more accurately measure the rate, was rechecked. Solution strengths were also redetermined.

It was thought that possibly carbon dioxide was escaping from the liquid samples while they were being drawn, since the liquid analysis showed less absorption than that indicated by the gas analysis. To avoid this possible loss, small diameter glass tubes about eight

inches long were drawn out to a fine tip and attached to the valves for liquid sampling. Long glass tubes, similar to Nessler tubes, with a volume of about fifty ml. were previously calibrated with a thirty-five ml. mark and filled with ten ml. of standard barium hydroxide and stoppered before the run. In taking a sample, the line was flushed and the sample tube raised until the tip of the glass tube extended just below the surface of the barium hydroxide. By filling to the mark, a 25 ml. sample was taken and contact with the air was minimized. However, no difference could be detected between this method and the one employed before; but due to the convenience of this method, it was adopted in all the future runs.

The humidity of the incoming air was determined with wet and dry bulb thermometers to eliminate the possibility of an increase in gas volume by picking up water vapor. The inlet air was found to be almost 100% saturated. Since it was desired to get only a material balance during these particular runs, tap water was used in runs seven and eight. The presence of magnesium in the water, however, gave a "fading" end-point which was undesirable.

Having checked the liquid and gas rate, there re-

mained to check the liquid and gas analytical methods. The possibility of hydrochloric acid reacting with the precipitated barium carbonate during the titration arose, and since the gas method of analysis was well established, this was investigated.

A group of 25 ml. samples were taken from the same solution of CO_2 in water. Ten ml. of standard barium hydroxide were added to each. The samples were then divided into three groups. The samples of series I were titrated directly to a phenolphthalein end point in the presence of the precipitate with hydrochloric acid. The samples of series II were centrifuged and a 25 ml. aliquot of the clear solution was titrated. The samples of series III were filtered through qualitative paper and 25 ml. of the clear filtrate was titrated. The results, expressed as ml. of acid required for back-titration, all calculated to a like basis are given in the following table. The figure is the average of all the runs in that series.

TABLE I

I	With Precipitate	3.11 ml.
II	Centrifuged	2.67 ml.
III	Filtered	2.45 ml.

These values indicate the necessity of removing the barium carbonate precipitate before adding acid. This procedure was adopted in run eleven and continued in all following runs.

In spite of this precaution in the analytical method, the gas analysis of run eleven indicated an absorption 63 per cent higher than that calculated from the liquid analysis. The gas analysis was checked by continuously bleeding a sample through standard barium hydroxide and measuring the volume of inert gas. Furthermore, the inlet composition could be calculated from the flow meter readings. In most cases these values checked within a small fraction of a per cent of CO_2 (0.1 % in some instances).

Assuming the gas analysis to be correct for run eleven, the concentration of carbon dioxide in the exit liquid was calculated to be 0.0001216 mols CO_2 per mol H_2O instead of .0000740, the measured value. From equilibrium data, the partial pressure of carbon dioxide in the gas above this theoretical solution would be 0.24 atmospheres. However, the actual pressure of CO_2 in contact with the exit liquid was only 0.207, indicating an impossibility, and showing that the values of gas concentration were in error.

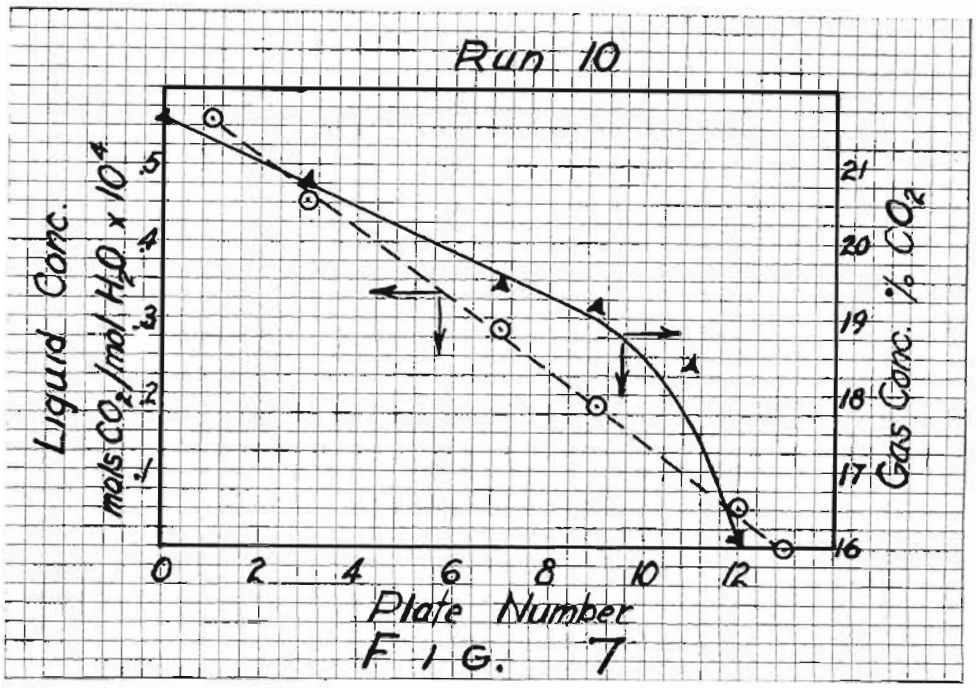

FIG. 7

A plot of gas and liquid concentrations against plate number gave further evidence as to the point of the discrepancy (see Fig. 7). In view of the fact that the liquid concentration changed linearly with plate number, the large change in gas concentration from plate eleven to twelve appears inconsistent.

Upon inspection of the tower itself, it was discovered that the down stream side of the orifice in the liquid inlet line was under reduced pressure and that air was being continuously introduced into the

system through the vent. This condition was due to the fact that the enlarged section below the orifice was not of sufficient diameter nor long enough to permit the bubbles to separate from the liquid. Hence, they were carried over and delivered directly on to plate 12 where these bubbles of air diluted the gas on this plate. This accounted for the apparently low value of CO_2 concentration in the exit gas and the sharp break in the curve of Fig. 7.

To correct this, the diameter of the enlarged section below the orifice was increased from 1½" to 2" standard pipe made considerable longer as shown in Fig. 2. On the next run, the pressure in this section was measured with a small manometer and found to be equal to atmospheric.

RUNS TWELVE TO SIXTEEN

The material balance of run number twelve checked to about 10 per cent, poorer than any of the subsequent runs.

There remained the necessity of devising a method of collecting gas samples continuously throughout the run which would eliminate the necessity of analyzing the gas during the run, eliminate the difficulty encountered when the gas samples were collected over

sodium sulfate solution, and also to enable a large number of samples to be collected.

This was accomplished by supporting the gas sample bottles above the bath and fitting each with a two hole stopper with glass tubes and pinch cocks as shown in figure 8. The bottles were first filled with distilled water, as was the bath. The lines were flushed out, then the bottles were attached as shown. When filled, the gas in the bottle was in contact

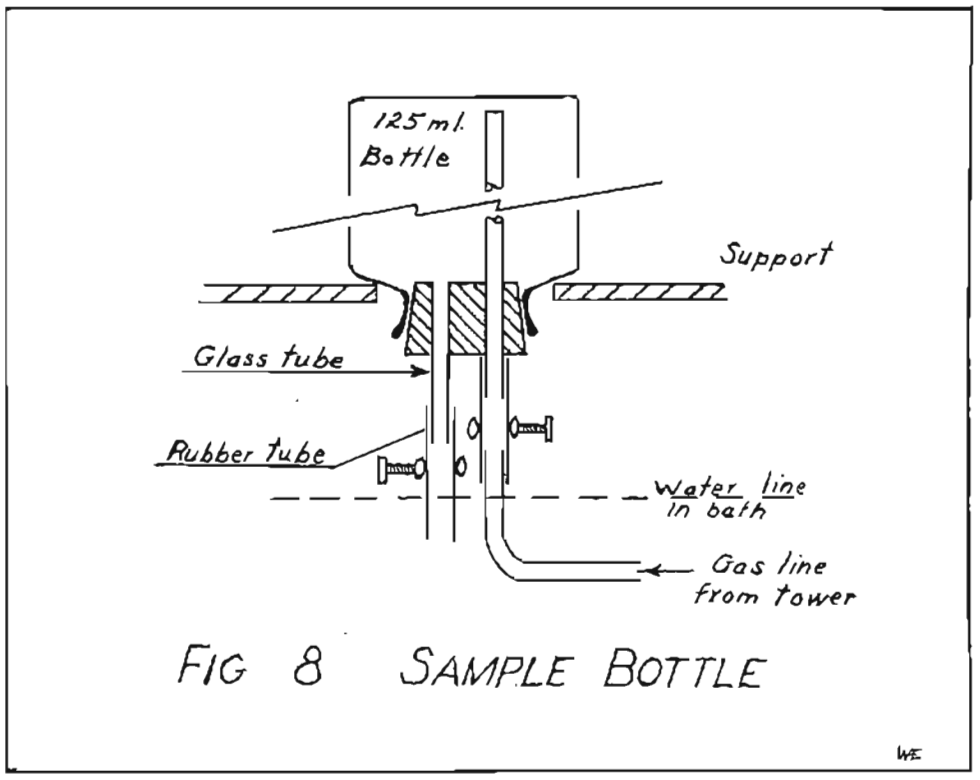

FIG 8 SAMPLE BOTTLE

with only a small area of the liquid in the bath.

The discharge liquid from run thirteen was caught in a drum. Air was blown through it for five hours. The CO_2 content had been reduced about 85% and its absorbing power was nearly 95% as much as freshly distilled water. This method of regeneration was used for the next three runs.

DIRECTIONS FOR OPERATION

The liquid storage drum should be filled long enough before-hand to allow the liquid to come to a constant temperature. Before the run, sufficient liquid sample tubes should be filled with ten ml. of approximately 0.05 normal barium hydroxide. Also, the gas sample bottles should be filled with distilled water and placed in the collecting rack, but not attached to the gas lines. After the CO_2 tank valve is warm, the run can begin.

Liquid and gas are started and adjusted to steady conditions, the liquid rate being controlled by the orifice and the gas rate by the valves and flow meters. Readings of temperatures and pressures are taken periodically, throughout the run. After twenty minutes of continuous operation, the gas lines are flushed by momentarily opening each valve. After this, the gas sample bottles are connected and

the rate in each adjusted to about one bubble per second. In this manner they can be taken continuously throughout the run. The liquid samples are collected by filling each tube to the 35 ml. mark. The liquid samples should be taken preferably by starting at the bottom and working up the tower.

One man is required to operate the valves regulating the gas flow. Another watches the inlet orifice meter, compensating from time to time for the drop of liquid head in the drum. He also times the gas meter revolutions, reads meter pressure, inlet liquid and outlet gas temperatures periodically. A third man reads outlet liquid and inlet gas temperatures and collects liquid samples. A fourth is responsible for pressure readings, collecting gas samples, and assists where needed.

RESULTS

DATA AND MATERIAL BALANCE

Table II contains the data from runs eleven through seventeen. In addition to that tabulated, the following experimental data was collected for run number sixteen:

Gas Meter pressure 1.15" Hg.

Time for two revolutions of gas meter 33.57 sec.

In figure 9 the number of ml. of 0.0507 normal hydro-

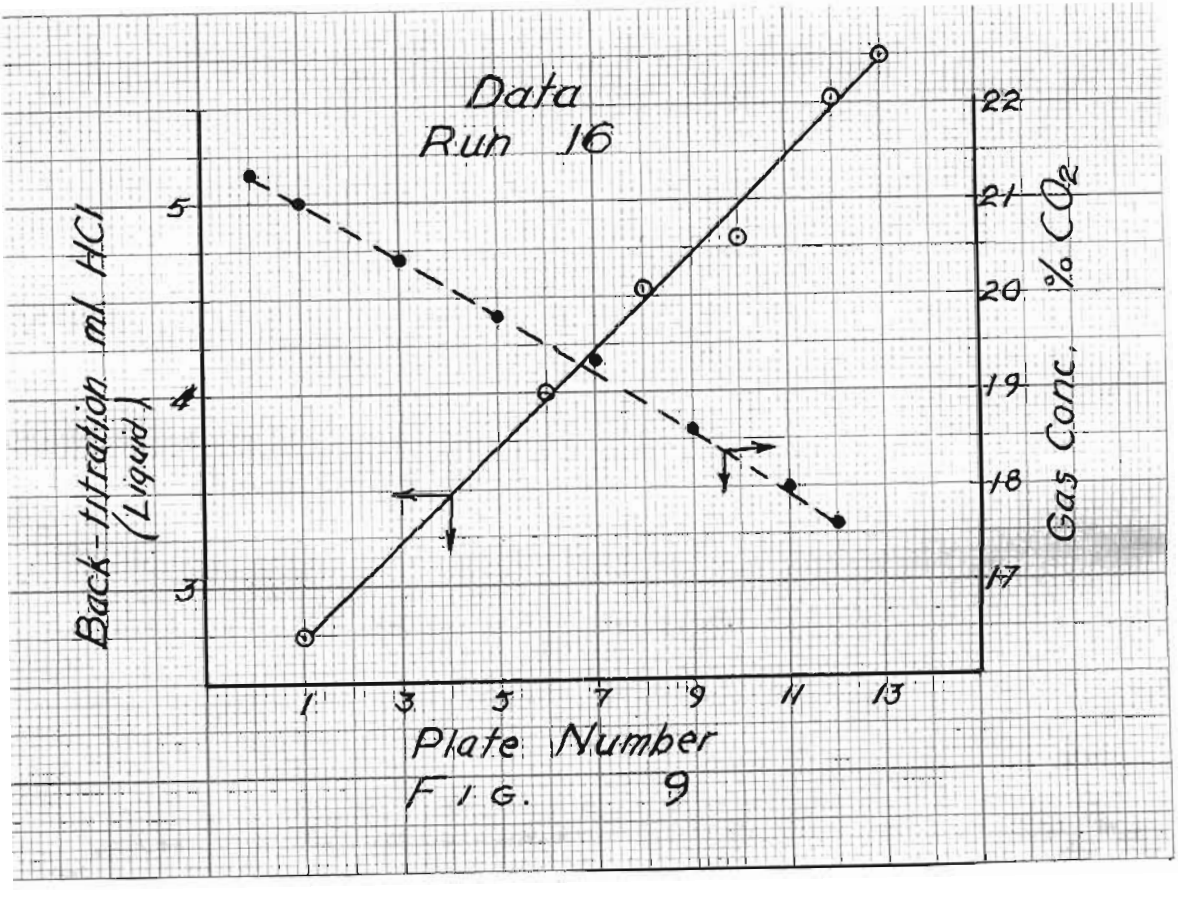

FIG. 9

TABLE II

DATA

Run	Temperature °C.				Pressure mm. Hg.			Inert Gas Rate Mols /hr.	Water Rate Mols /hr.	Gas % CO_2		Liquid Conc.*	
	Gas		Liquid										
	in	out	in	out	Top	Bot.	Bar.			in	out	in	out
11	26.0	25.5	31.8	31.6	3.0	19.0	736.8	0.0532	39.4	21.3	17.8	0.0	0.740
12	26.0	29.8	31.0	30.5	3.0	18.0	733.1	0.0465	39.4	21.3	17.5	0.0	0.801
13	26.3	28.9	28.7	29.0	0.8	16.4	740.1	0.0530	39.4	21.4	17.5	0.0	0.800
14	28.3	29.4	28.5	28.7	4.4	20.2	731.7	0.0524	39.4	22.5	17.8	0.119	0.891
15	25.3	29.0	28.0	27.2	4.7	17.9	726.0	0.0530	39.4	21.4	16.6	0.119	0.880
16	28.0	31.0	30.7	29.5	4.2	20.5	743.8	0.0535	39.4	21.3	17.6	0.108	0.872
17	26.3	27.0	27.0	27.0	4.7	22.1	738.2	0.0534	40.1	21.6	18.7	0.164	0.777

Note: Run 17 was made using "Lupomin"

* Liquid concentration is in mols CO_2 per mol H_2O x 10^4

chloric acid required to titrate the excess hydroxide is plotted against the plate number from which the sample was drawn. Also the carbon dioxide concentration of the gas sample was plotted against plate number.

CALCULATION OF ABSORPTION FROM LIQUID DATA

Since the top liquid sample required 5.48 ml. of acid and the bottom 2.49 ml.--

$$(5.48 - 2.49)\ \frac{35}{25} \times \frac{0.0507}{1000} \times \frac{1000}{25} \times \frac{1}{2 \times 55.55} = 0.0000764 \text{ mols}$$

CO_2 absorbed per mol H_2O and:

$$0.0000764 \times \frac{11.83}{18} = 0.0000502 \text{ mols } CO_2 \text{ absorbed per}$$

minute as calculated from the liquid analysis.

CALCULATION OF ABSORPTION FROM GAS DATA

Two revolutions of the gas meter indicate 0.2 cubic feet, then, times the calibration factor, 1.027, we get:

$$0.2 \times 1.027 \times \frac{60}{33.57} = 0.367 \text{ cubic feet wet air at meter}$$

conditions in per minute. At the liquid temperature the vapor pressure of water is 31.5 mm. Therefore:

$$\frac{0.367}{359} \times \frac{(744 + (1.15 \times 25.4) - 31.5)}{760} \times \frac{273}{301} = 0.000899$$

mols dry air (inert gas) in per minute. The gas concentration changes from 21.3% to 17.6%.

$$\frac{0.000899}{0.787} \times 0.213 = 0.000243 \text{ mols } CO_2 \text{ in}$$

$$\frac{0.000899}{0.824} \times 0.176 = \frac{0.000192 \text{ mols } CO_2 \text{ out}}{0.000051 \text{ mols } CO_2 \text{ absorbed per min}}$$

as calculated from the gas analysis. This checks the figure of 0.0000502 from the liquid analysis within 1.6 % which is entirely satisfactory.

EQUILIBRIUM DATA

In order to ascertain the absorption which might be expected, it was necessary to have equilibrium data for the system CO_2-H_2O. Buch[1] tested Henry's law for this system and found that it held very well in the range from one atmosphere to 0.00005 atmospheres. The values for K (Henry's law constant) for various temperatures used were those recorded by Quinn and Jones[2]. The equilibrium lines for the system at 20, 25, and 30 degrees C. are plotted in figure 10. Also the equilibrium points of Morgan and Maass[3] are plotted for solutions in contact with CO_2, with a partial pressure below one atmosphere.

Number of Theoretical Plates

In figure 11 the equilibrium curve is plotted as mols CO_2 per mol water against mols CO_2 per mol inert gas. The operating line, which was drawn in the same plot, was obtained as follows:

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1. Buch,K. III Nord Kemistmotet (Finland) p. 184-92 (1928). Chem. Abst. 23, 2632 (1929)

2. Quinn,E.L., and Jones,C.L., "Carbon Dioxide", New York, Reinhold Pub. Co. (1936) p. 94

3. Morgan,O.M., and Maass,O., Can. J. Research 5, 162-99 (1931)

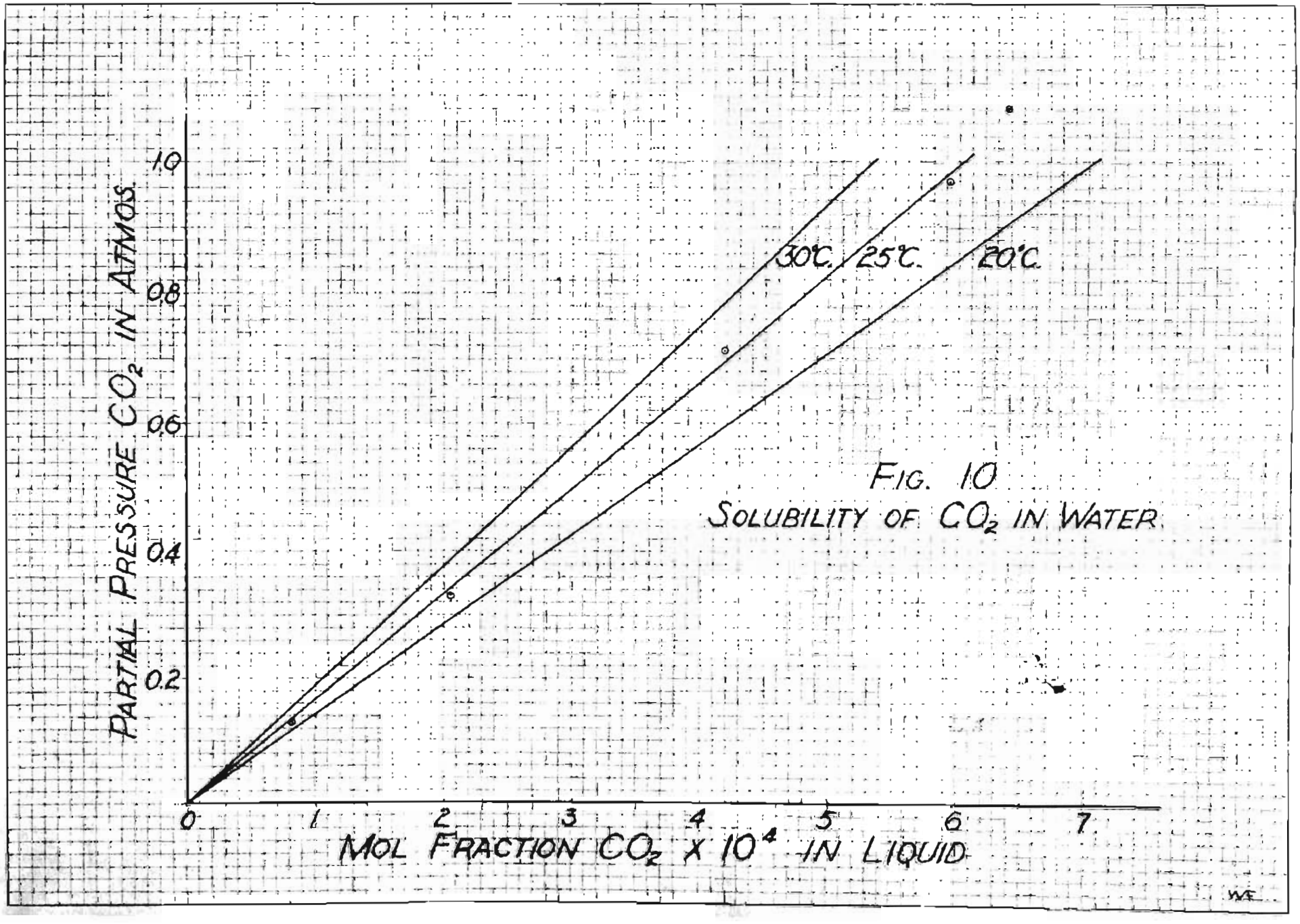
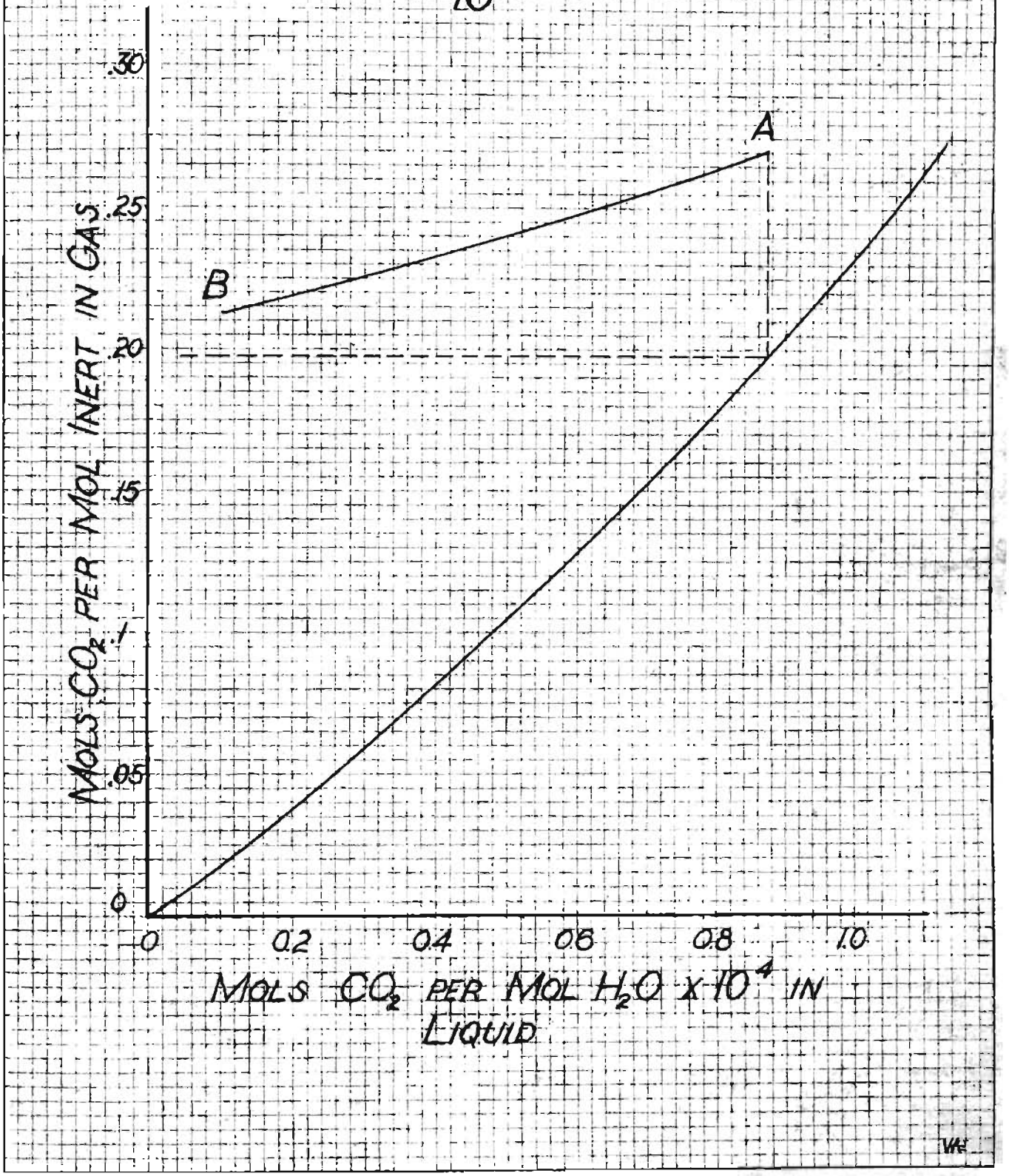


FIG. 10
SOLUBILITY OF CO_2 IN WATER

FIG. 11
EQUILIBRIUM AND OPERATING LINE FOR RUN 16



Liquid in at 0.0000108 mols CO_2 per mol water.

Gas out at 17.6% CO_2 = 0.2136 mols CO_2 per mol inert.

Thus 0.0000108, 0.2136 are the coordinates of point "B" (figure 11) representing the top of the tower. Likewise, 0.0000872, 0.271 are the coordinates of point "A", the bottom of the tower. The usual step-wise procedure (indicated by the dotted lines) for determining the number of theoretical plates required for the absorption, shows about one theoretical plate needed. Thus, by dividing by twelve actual plates, a plate efficiency of about 8.3 per cent is obtained. This checks the results of Whitman and Davis[1] who were absorbing carbon dioxide in a bubble plate tower with sodium carbonate solution.

CALCULATION OF K_La.

The following calculations for run sixteen are typical of the method. The driving force can be obtained from the plot in Figure 11. For the bottom of the tower it is the horizontal distance between point "A" and the equilibrium curve, or:

$(1.12 - 0.871) \times 10^{-4} = 0.249 \times 10^{-4}$ mols CO_2 per mol water.

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1. Whitman,W.G., and Davis,G.H.B., "A Comparison of Gas Absorption and Rectification", Ind. Eng. Chem., 18, 264-6 (1926)

Likewise, the driving force at the top is:

$(0.925 - 0.106) \times 10^{-4} = 0.819 \times 10^{-4}$ mols CO_2 per mol water.

Logarithmic mean driving force =

$$\frac{(0.819 - 0.249) \times 10^{-4}}{2.302 \log \frac{0.819}{0.249}}$$

$= 0.479 \times 10^{-4}$ mols CO_2 per mol water.

Tower volume = 1.57 cubic feet. (superficial)

Mols CO_2 absorbed per hour $= 30.12 \times 10^{-4}$

Therefore, $K_La = \frac{30.12 \times 10^{-4}}{1.57 \times 0.479} \times 10^{-4} = 40.1$ mols CO_2 absorbed per hour per cubic foot per unit driving force (in mols CO_2 per mol water)

The values of K_La were calculated for run eleven to sixteen inclusive. For comparison, the values of K_La were calculated from the data of those investigators using the CO_2 - water system. Sherwood, Draemel, and Ruckman[1], who were using a packed tower of 18 inch diameter, report that K_La varies as the 0.88 power of the water rate expressed in pounds per hour per square foot. The other investigators used glass towers with small cross sectional areas. Although this relation

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1. Sherwood, T.K., Draemel, F.C., and Ruckman, N.E., "Desorption of CO_2 from Water in a Packed Tower", Ind. Eng. Chem., 29, 282-5 (1937)

of K_La to liquid rate given by Sherwood is not exact in the case of small diameter towers, it is probably the best method for comparing results. Hence all values were corrected to the liquid rate used in the present work. (2034 lbs. per hr. per sq. ft.) These values are tabulated in Table III.

TABLE III

Tower Absorption Coefficients

Run	Equipment	Tower Diam. in.	Temp. deg. C.	K_La
11	Bubble plate	8.0	31.7	34.8
12	Bubble plate	2	30.7	40.2
13	Bubble plate	2	28.9	34.9
14	Bubble plate	2	28.6	37.7
15	Bubble plate	2	27.6	39.4
16	Bubble plate	2	30.1	40.1
Sherwood et al	1" carbon ring	18.0	23.9	59.0
Simmons and Osburn	Raschig rings	3.58	10.4	26.2
Payne and Dodge	glass rings	2.84	25.0	20.8
Cantelo et al	Raschig rings	3.58	7.0	8.7
17*	Bubble plate	8.0	27.0	21.2

*Run 17 was made using addition agent "Lupomin".

The values of K_La determined in this work are in fair agreement among themselves and are of the same order at magnitude as those of other investigators. The differences are largely due to variations in operating conditions. Temperature affects the coefficient. K_La is also a function of liquid rate and even though the values have been corrected to a similar water rate, data from small towers, under eight inches in diameter, have been found not to be applicable to larger equipment.

For comparison, the best value is probably that of Sherwood which indicates that the bubble plate tower is less efficient than a packed tower. This is some what out of line, in as much as bubble plate towers are especially adapted to the case of liquid film controlling. However, where this type of equipment does exist, it can be operated with efficiencies at least comparable with other types. The higher initial cost and larger pressure drop account for their limited use.

THE EFFECT OF SURFACE TENSION ON THE RATE OF ABSORPTION

If we consider a gas molecule moving from the gas phase into the liquid phase, it seems possible that the physical properties of the liquid at the interface could affect the rate of transfer. Viscosity has been correlated with rate of absorption for the case of CO_2 in hydroxide and carbonate by Hitchcock and Cadot[1]. Riou[2] and co-workers changed the viscosity of the absorbing liquids by adding inert substances such as glycol, glycerine, and alcohol. They concluded that viscosity was not a controlling factor in the absorption rate. However the change of surface tension resulting from these addition agents and the possible effect upon absorption was not mentioned.

Closer investigation of the data of Riou shows that in the cases mentioned above where the rate was increased by addition agents the surface tension was reduced. For example, in the case of ethanol, the surface tension was decreased about 30% and the rate of absorption increased 30% although the viscosity was increased over the same range of concentration.

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1. Hitchcock, L.B., and Cadot, H.M., "Rate of Absorption of CO_2", Ind. Eng. Chem., 27, 728-32 (1935)

2. Riou, Paul and Cartier, Paul, "Influence of Viscosity on Rate of Absorption of CO_2 by Means of Neutral Sodium Carbonate Solutions", Compt. rend., 186, 1727-9 (1937)

Killeffer[1] used such agents as formaldehyde and methyl alcohol in carbonate solutions to absorb CO_2 and reports increases of 115% and 20% respectively. Williamson and Mathews[2] absorbed CO_2 in K_2CO_3 solution. They report than an "alcoholic solution" increased the rate 40%. Uhlig[3] developed equations for the work involved when a gas molecule was absorbed by consideration of free energy changes, diameter of molecules, and surface tension. He showed clearly the relation of surface tension of the liquid and gas solubility.

It appeared plausible that a high surface tension would have a retarding effect on the gas molecules. Since most of the above mentioned agents give only a relatively small decrease in surface tension and with the introduction of newer, powerful surface active agents such as Aerosol O.T. it was decided to make a preliminary investigation of this effect.

It was found that a 0.1% solution of Aerosol O.T. in water foamed so much as to make it unusable in a tower. Attempts to find a successful defoaming agent

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1. Killeffer,D.H., "Absorption of CO_2", Ind. Eng. Chem., 29, 1293 (1937)

2. Williamson,R.V., and Mathews,J.H., "Rate of Absorption and Equilibrium of CO_2 in Alkaline Solutions", Ind. Eng. Chem., 16, 1157-61 (1924)

3. Uhlig,H.H., "The Solubility of Gases and Surface Tension", J. Phys. Chem., 41, 1215 (1937)

failed.

Another surface active agent, Lupomin[1], was secured which did not foam appreciably. It is an organic acid salt of amido amino alcohol. In run 17 all conditions were essentially the same as in the previous runs as shown by Table II. The liquid in the tower was about 0.01% solution and had a surface tension of 33 dynes per cm. (water at same temperature equals 72.6). The liquid rate was increased slightly, due to the effect of the lowering of surface tension on the orifice coefficient.

However, in place of the 0.00301 mols CO_2 absorbed per hour in run 16, this run showed 0.00246 mols absorbed per hour. Likewise the absorption coefficient, K_La , was only 21.2 as compared with 39.1, the average for the three preceding runs as tabulated in Table III.

The adverse effect could be explained by the fact that these large organic molecules might collect at the surface and thereby possibly block much of the area available for diffusion. A liquid which, in itself possesses a low surface tension may give the desired effect. Other agents may accomplish the result. It might be pointed out that the high rate of absorption

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1. J. Wolf and Company, Possaic, New Jersey

of the rather viscous ethanol amines may be due, in part, to their low surface tension.

The subject is not closed. Much work remains to be done. It is difficult to conceive of diffusion taking place with out being affected by both surface tension and viscosity. Furthermore, there are undoubtedly other factors not yet considered. Especially important is chemical reaction or association of the gas molecules with the solvent. It has been pointed out that the optical rotation of a carbonate solution with the addition of glucose as an "inert" to vary viscosity, continued to change for several hours.

SUMMARY

1. A twelve plate distillation tower was converted into a gas absorber. Auxillary equipment was designed and constructed.

2. Experimental runs were made, using the system CO_2 - water to determine the performance. Results have been expressed as K_La, the volumetric coefficient of absorption.

3. An examination of existing data was made in an attempt to correlate the effect of surface tension upon rate of gas absorption.

4. An experimental run, made by using 0.01% solution of Lupomin which reduced the surface tension from 72.6 to 33, did not give an increase in rate of absorption as expected.

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